

PACENT COOPERATION TREATY

PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To:

PARK, Jang-Won
Jewoo Building 5th floor, 200,
Nonhyun-dong, Kangnam-ku
Seoul 135-010
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 29 September 2000 (29.09.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference PAKIST00320	International application No. PCT/KR00/00984

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY (for all designated States except US)
KIM, Yoon-Ho et al (for US)

International filing date : 30 August 2000 (30.08.00)
Priority date(s) claimed : 03 May 2000 (03.05.00)
Date of receipt of the record copy
by the International Bureau : 13 September 2000 (13.09.00)
List of designated Offices :

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE
National : CN, IN, JP, US

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
☒ confirmation of precautionary designations
☐ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

Anman QIU

Telephone No. (41-22) 338.83.38

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INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Record Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is **20 MONTHS** from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, **30 MONTHS** from the priority date, provided that the election is made before the expiration of 19 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. It is **the applicant's responsibility** to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.

GR and ES became bound by PCT Chapter II on 7 September 1996 and 6 September 1997, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1996 and 6 September 1997, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit is the filing date of the earliest application whose priority is claimed.

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PARENT COOPERATION TREATY

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From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)


To:

PARK, Jang-Won
Jewoo Building 5th floor, 200,
Nonhyun-dong, Kangnam-ku
Seoul 135-010
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 29 September 2000 (29.09.00)	
Applicant's or agent's file reference PAKIST00320	IMPORTANT NOTIFICATION
International application No. PCT/KR00/00984	International filing date (day/month/year) 30 August 2000 (30.08.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 03 May 2000 (03.05.00)
Applicant KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed to Rule 17.1(c)** which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed to Rule 17.1(c)** which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
03 May 2000 (03.05.00)	2000/23676	KR	13 Sept 2000 (13.09.00)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer Anman QIU  Telephone No. (41-22) 338.83.38
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PATENT COOPERATION TREATY

WO 01/83395
PCT/KR00/00984

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

PARK, Jang-Won
Jewoo Building 5th floor, 200,
Nonhyun-dong, Kangnam-ku
Seoul 135-010
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 08 November 2001 (08.11.01)		IMPORTANT NOTICE	
Applicant's or agent's file reference PAKIST00320			
International application No. PCT/KR00/00984	International filing date (day/month/year) 30 August 2000 (30.08.00)	Priority date (day/month/year) 03 May 2000 (03.05.00)	
Applicant - KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY et al			

1. Notice is hereby given that the International Bureau has **communicated**, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this notice:

US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

CN,EP,IN,JP

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on 08 November 2001 (08.11.01) under No. WO 01/83395

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and the PCT Applicant's Guide, Volume II.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer <p style="text-align: center;">J. Zahra</p>
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**LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC
CERAMIC COMPOSITIONS AND METHOD THEREOF**

TECHNICAL FIELD

The present invention relates to a low temperature sinterable and low
5 loss dielectric ceramic compositions for use in fabricating various high
frequency devices such as a multilayer chip capacitor, a multilayer chip filter,
a multilayer chip capacitor inductor composite device and module, a low
temperature sinterable substrate, a resonator or a filter and a ceramic antenna,
and its method.

BACKGROUND ART

Recently, with the rapid development in a mobile communication and a
satellite communication, a high frequency dielectric ceramics is in a high
demand as a material for a high frequency integrated circuit or a dielectric
15 resonator.

Major characteristics of the dielectric ceramics used for a high frequency
includes a high dielectric constant (ϵ_r), a quality factor (Q) and a stable and
tunable temperature coefficient (τ_f) of a resonance frequency.

Representative high frequency dielectric compositions which have been
20 widely known up to now are (Zr, Sn)TiO₄ group, BaO-TiO₂ group, (Mg,
Ca)TiO₃ group, and Ba-(Zn_{1/3}Ta_{2/3})O₃, Ba(Mg_{1/3}Ta_{2/3})O₃, Ba(Zn_{1/3}Nb_{2/3})O₃ as Ba-
perovskite group etc.

However, these compositions are disadvantages in that they are mostly

fired at a high temperature of 1,300~1,500°C, phase synthesis is not easy, a dielectric constant is low or a high-priced material should be used.

Besides, lately, advancement of a portable information communication devices lead to development of various types of substrates and multi-chip module (MCM) by a multilayer chip high frequency devices or low temperature co-firing ceramics (LTCC), and a research and development of a low temperature firing high performance high frequency ceramics are conducted accordingly.

However, there are problems that the performance of the high frequency characteristic is considerably degraded such as, for example, most of them are not sufficient in terms of density when being fired at a low temperature, a dielectric constant is decreased according to addition of a sintering aid, a quality factor is degraded and a temperature factor is changed.

In addition, silver or copper conduct with a small high frequency loss and a cofiring available low temperature firing high frequency dielectric ceramic are very rare.

Therefore, an object of the present invention is to provide a dielectric ceramics composition which can be fired at a very low temperature but has an excellent high frequency dielectric characteristic of various temperature compensation characteristics according to a high quality factor, a dielectric constant, a stable temperature factor and a composition, and can be implemented at a low cost.

Another object of the present invention is to provide a dielectric ceramics

composition which can employ Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

DETAILED DESCRIPTION OF THE INVENTION

In order to achieve the above objects, there is provided a dielectric ceramics composition which is constructed by combining 1 mole of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ ($0 \leq y \leq 0.6$) as a main component, one of 0~5 wt % B_2O_3 , 0~5 wt % H_3BO_3 , 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass is added as an additive thereto, and fired at a low temperature of 800~925°C, its preparation method, and a high frequency dielectric ceramics device using the same. In this respect, 'M' is one of Mg, Co, Ni, 'x' is $0 \leq x \leq 0.55$ in case of Mg and 'x' is $0 \leq x \leq 1$ in case of Co, and $0 \leq x \leq 1$ in case of Ni

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing a phase dissociation temperature of $(Zn_{1-x}M_x)TiO_3$ according to the substituted amount of Mg.

MODE FOR CARRYING OUT THE PREFERRED EMBODIMENTS

The present invention will now be described with reference to

accompanying drawings.

A high frequency dielectric ceramics composition of the present invention is characterized in that it has a very low firing temperature (800~925°C) compared to that of a conventional dielectric composition, has an excellent high frequency dielectric characteristic of various temperature compensation characteristics ($\tau f = -52 \sim +104$ ppm/°C) according to a high quality factor ($Q \times f = 12,000 \sim 84,000$ GHz), a dielectric constant ($16 \leq \epsilon_r \leq 32$), a stable temperature factor and a composition, and can be implemented with a low-priced material such as ZnO, MgO, CoO, NiO, TiO₂,

In addition, the high frequency dielectric ceramics composition of the present invention is also characterized in that it employs Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature firing substrate, a resonator and a filter or a ceramic antenna.

In the present invention, the low temperature firing composition of the present invention has an excellent quality factor (close to the existing high temperature firing composition) more than several times the existing one. In addition, in the claimed composition coverage, combination of composition having an excellent high frequency characteristic of the almost infinite number can be obtained compared to any of the conventional ones.

ZnTiO₃ (crystal structure has a rhombohedral symmetry) is phase-dissociated to Zn₂TiO₄ (cubic symmetry) and TiO₂ (rutile) at a higher

temperature than 945°C (refer to Fig.303 of Phase Diagrams for Ceramist by the American Ceramic Society, System ZnO-TiO₂ by Dulin and Rase), and thus, it is very difficult to be prepared.

In order to obtain a pure ZnTiO₃, phase synthesis and firing must be made at a below 945°C. A preliminary experiment of the present invention shows a result through an X-ray diffraction analysis that phase dissociation starts at near 925°C so that a thermal treatment must be performed at below 925°C.

In a preferred embodiment of the present invention, in order to remove the shortcomings, Zn²⁺, a positive ion of A-site constituting an ABO₃ type ilmenite phase ceramics, is substituted with Mg²⁺ (up to 0.55 mole), to thereby enlarge a thermal stabilization temperature of ZnTiO₃ to a high temperature range (refer to Figure 1), so that the preparation process coverage is widened and the high frequency dielectric characteristic are highly improved.

Figure 1 is a graph showing a phase dissociation temperature of (Zn_{1-x} Mg_x)TiO₃ according to the substituted amount of Mg. In case that a region x = 0, ZnTiO₃ is dissociated at a temperature of 945°C, and since the dissociation temperature goes up to a high temperature by the substitution of Mg, a single phase of the (Zn_{1-x} Mg_x)TiO₃ solid solution can be synthesized or fired even at a temperature of higher than 945°C.

Accordingly, a single phase can be obtained anywhere in the region II of Figure 1, which is the phase synthesis region of the present invention.

A high frequency dielectric ceramics composition in accordance with a

preferred embodiment of the present invention will now be described.

Powders (an average particle diameter is $1\mu\text{m}$) of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 (>99%) was weighed according to a composition range of $(\text{Zn}_{1-x}\text{M}_x)\text{TiO}_3$ and $y\text{TiO}_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.55$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.6$), mixed in a wet ball mill method, dried at 120°C , and calcined and synthesized at a temperature of $850\sim 950^\circ\text{C}$ for four hours.

The calcined powder was mixed with 0.5 wt % B_2O_3 , 0~5 wt % $\text{SiO}_2\text{-K}_2\text{O}$ glass and a combination of 0~10 wt % B_2O_3 and $\text{SiO}_2\text{-K}_2\text{O}$ as a sintering aid.

At this time, in case of B_2O_3 , besides the oxide, a water soluble boron (H_3BO_3) was used to improve homogeneity in adding a little amount.

Solubility (per water 100cc) of boron to cool water (30°C) and hot water (100°C) is 6.35 and 27.6 (refer to Handbook of Chemistry and Physics, 55th ed., CRC Press, 1974-75).

In case of the present invention, cool water was used to make boron corresponding to the solubility to an aqueous solution, into which the main component or the main composition and the glass powder are mixed and crushed.

In crushing, since the temperature of slurry goes up further (especially, up to 45°C in case of high speed centrifugal crushing), the mixture of boron can be more uniform.

As for the $\text{SiO}_2\text{-K}_2\text{O}$ glass, SiO_2 and K_2CO_3 were mixed with K_2CO_3 by 55~75 wt % and 25~45 wt %, melt at a temperature of $1100\sim 1200^\circ\text{C}$, quenched

at cool deionized water, ball-milled for 24 hours, thereby obtaining glass powder, and it was confirmed that an amorphous phase of glass was obtained according to an X-ray diffraction analysis result.

Since the present invention is aimed at a low temperature firing at a
5 below 925°C, in order to obtain fine powder (average particle diameter of below 0.5µm) less than submicron, a stabilized zirconia ball with a diameter of 2mm was used and crushed for four hours by an attrition mill, or a fine stabilized zirconia ball with a diameter of 1mm was used and subjected to a high speed centrifugal crushing for 5~10 minutes.

10 An aqueous solution to which 2 wt % PVA binder was added is mixed with the dried powder to make a granule of about 150µm and shaped to a disk test sample having a diameter of 8mm and a thickness of 3.8mm at a pressure of 98 Mpa.

The shaped test sample was maintained at a temperature of 300~500°C
15 for over 3 hours to burn out the binder, and then sintered at a temperature 800~925°C at an atmosphere.

At this time, a heating rate was 10°C/min. The sintered test sample was ground with an SiC polishing paper (#1,500) to obtain about 0.45 ratio of diameter to thickness of the test sample.

20 The high frequency dielectric characteristic was measured in a TE₀₁₈ mode by using a network analyzer (HP 8720C) by making a cylindrical dielectric ceramics resonator, and a dielectric constant was measure by a Hakki-Coleman method, a quality factor was measure by an open cavity method, a

temperature factor of a resonance frequency was measured by an invar cavity at a temperature range of +20~+70°C.

Table 1 shows a high frequency dielectric characteristic in case that B_2O_3 , boron (H_3BO_3) and a combination component of boron and SiO_2-K_2O glass are added as sintering aids to a main composition that $x=0.01$ and $y=0.12$ among $(Zn_{1-x}M_x)TiO_3$ ($0 \leq x \leq 0.55$) and $yTiO_2$ ($0 \leq y \leq 0.6$) composition.

In Table 1, a 800°C-sintered body had about more than 92% relative density, and 875°C-sintered body had about more than 97% relative density.

In the embodiments 2~5 and 6~10, it is noted that quality factor was further improved in case of adding boron instead of adding B_2O_3 , and as for the temperature coefficient, the variation rate according to the sintering temperature (800°C and 875°C) was smaller. This effect results from a uniformity of boron.

As the sintering characteristic thanks to addition of B_2O_3 , the dielectric constant and quality factor were much increased, and were increased up to about 2 wt % and then reduced at 5 wt %.

The temperature coefficient was moved to a positive as the amount of B_2O_3 is increased.

Accordingly, in the embodiments of Table 1, it is anticipated that if the value 'y' is a bit increased more than 0.2 and the amount of additive is controlled, an excellent dielectric property of which the temperature factor is almost '0' can be obtained.

That is, in order to be a usable high frequency characteristic, not only TiO_2 , but the amount of additive needs to be controlled property, and

accordingly, various composition groups can be obtained.

Table 1: High frequency dielectric property of a dielectric resonator fabricated with composition of $(\text{Zn}_{0.99}\text{M}_{0.01})\text{TiO}_3$ ($\text{M}=\text{Mg}$) + 0.2TiO_2 + $(\text{B}_2\text{O}_3$,

5 H_3BO_3 , or H_3BO_3 + SiO_2 - K_2O glass)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	SiO_2 - K_2O glass (wt%)	Sintering temperat- ure ($^{\circ}\text{C}$)	Dielectric constant (ϵ_r)	Quality factor ($Q \times f$ GHz)	Temperature coefficient (τ_f :ppm/ $^{\circ}\text{C}$)
1	-	-	-	800	13.8	22900	-22
				875	21.1	32400	-50
2	0.25	-	-	800	22.3	65700	-52
				875	26.9	78200	-48
3	0.50	-	-	800	23.0	54800	-43
				875	26.4	84600	-40
4	1.00	-	-	800	19.7	50100	-44
				875	26.5	80900	-33
5	2.00	-	-	800	19.6	44800	-29
				875	27.2	79300	-22
6	-	0.25	-	800	22.1	59800	-46
				875	27.0	84300	-43
7	-	0.50	-	800	20.2	50600	-44
				875	26.0	85200	-39

8	-	1.00	-	800	19.3	47700	-33
				875	26.3	81200	-34
9	-	2.00	-	800	19.5	45400	-40
				875	26.7	70100	-20
10	-	5.00	-	800	16.5	40000	-10
				875	25.1	60200	+20
11	-	0.50	0.50	800	19.5	58800	-43
				875	25.8	67200	+39
12	-	0.50	1.00	800	17.0	42400	-20
				875	23.6	58400	-38
13	-	0.50	2.00	800	16.7	26300	-17
				875	23.8	45100	-36
14	-	0.50	3.00	800	15.4	25000	-21
				875	24.1	36200	-29
15	-	0.50	5.00	800	13.7	19100	-19
				875	23.4	24500	-43

Table 2 indicates a dielectric property in case of increasing the amount of Mg and TiO_2 ($x = 0.55$, $Y = 0.6$).

- 5 Table 2: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(\text{ZnO}_{0.45}\text{M}_{0.55})\text{TiO}_3$ ($\text{M}=\text{Mg}$) + 0.6TiO_2 + (B_2O_3 , H_3BO_3 , or $\text{H}_3\text{BO}_3 + \text{SiO}_2\text{-K}_2\text{O}$ glass)

No.	B ₂ O ₃ (wt%)	H ₂ BO ₃ (wt%)	SiO ₂ - K ₂ O glass (wt%)	Sintering temperat- ure (°C)	Dielectric constant (ϵ_r)	Quality factor (Qxf GHz)	Temperature coefficient (τ_f :ppm/°C)
16	-	-	-	900	20.2	18300	+60
				925	24.3	20700	+56
17	0.25	-	-	900	26.9	19700	+54
				925	30.1	35300	+78
18	0.50	-	-	900	26.9	20300	+57
				925	29.5	44000	+65
19	1.00	-	-	900	26.0	22300	+51
				925	28.4	35300	+87
20	2.00	-	-	900	25.7	22400	+57
				925	28.6	30500	+79
21	-	0.25	-	900	27.3	23200	+72
				925	30.1	58900	+86
22	-	0.50	-	900	26.5	23000	+72
				925	29.3	46000	+70
23	-	1.00	-	900	25.3	23100	+55
				925	28.2	33400	+73
24	-	2.00	-	900	25.5	21700	+68
				925	28.1	27300	+88
25	-	5.00	-	900	23.7	21200	+75

				925	27.5	16600	+104
26	-	0.50	0.50	900	22.8	27900	+54
				925	26.8	22700	+79
27	-	0.50	1.00	900	24.2	29800	+46
				925	29.0	26800	+76
28	-	0.50	2.00	900	28.4	22300	+65
				925	32.0	17900	+71
29	-	0.50	3.00	900	28.9	27600	+49
				925	32.5	19500	+84
30	-	0.50	5.00	900		21200	+33
				925		11900	+53

In the above embodiments, positive temperature coefficients were obtained. In this case, a temperature coefficient of '0' can be naturally obtained by adequately reducing the amount of TiO_2 .

5 Meanwhile, in case that $x > 0.55$, the dielectric constant and the quality factor were much degraded than those of the present invention, and most of all, the sintering characteristic is degraded as the amount of Mg is increased.

Table 3 indicates a composition exhibiting an excellent dielectric property with a temperature coefficient of '0' on the basis of Table 1 and Table 2.

10 Table 3: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(\text{Zn}_{0.70}\text{M}_{0.30})\text{TiO}_3$ ($\text{M}=\text{Mg}$) + 0.2TiO_2 + (B_2O_3 , + SiO_2 - K_2O glass)

No.	B ₂ O ₃ (wt%)	SiO ₂ -K ₂ O glass (wt%)	Sintering temperat- ure (°C)	Dielectric constant (ϵ_r)	Quality factor (Qxf GHz)	Temperature coefficient (τ_f :ppm/°C)
31	-	0.50	925	16.6	26900	-16
32	0.25			24.5	65300	-11
33	0.50			24.9	69700	-6
34	1.00			24.7	74700	-10
35	1.50			24.4	69000	-1
36	2.00			24.2	67300	-5
37	-	1.00	925	17.1	27200	-27
38	0.25			24.8	58500	-14
39	0.50			25.0	59200	-7
40	1.00			25.0	59300	-2
41	1.59			24.7	55400	0
42	2.00			24.5	55800	+1
43	-	2.00	925	18.3	20300	-14
44	0.25			25.1	52200	-9
45	0.50			25.2	52700	-4
46	1.00			25.0	55700	+5
47	1.50			25.3	48100	+2
48	2.00			24.9	50800	+14

No.	B ₂ O ₃ (wt%)	SiO ₂ -K ₂ O glass (wt%)	Sintering temperat- ure (°C)	Dielectric constant (ϵ_r)	Quality factor (Qxf GHz)	Temperature coefficient (τ_f :ppm/°C)
49	-	3.00	900	17.6	25400	-24
50	0.25			21.9	33600	-20
51	0.50			23.8	39100	-10
52	1.00			25.6	38400	+17
53	1.50			25.6	44800	+20
54	2.00			25.5	42100	+26
55	-	5.00	900	19.5	19500	-17
56	0.25			21.8	27100	-20
57	0.50			22.8	30700	-32
58	1.00			23.9	31600	-11
59	1.50			25.0	36800	+24
60	2.00			25.1	37700	+31

In the embodiments 32~60, an excellent dielectric property with a dielectric constant of more than 24, a quality factor of more than 50000 and a temperature factor of ± 30 ppm/°C was obtained from the combination of less than 2 wt % B₂O₃ (or H₃BO₃) and SiO₂-K₂O glass.

Table 4 shows an influence of B₂O₃ and H₃BO₃ additive for the composition of (Zn_{0.70}Mg_{0.30})TiO₃ and 0.2TiO₂.

Table 4: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(\text{Zn}_{0.70}\text{M}_{0.30})\text{TiO}_3$ ($\text{M}=\text{Mg}$) + 0.2TiO_2 + (B_2O_3 , or H_3BO_3)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	Sintering temperat- ure ($^{\circ}\text{C}$)	Dielectric constant (ϵ_r)	Quality factor (Qxf GHz)	Temperature coefficient (τ_f :ppm/ $^{\circ}\text{C}$)
61	-	-	900	19.3	51200	-31
			925	22.5	84400	-29
62	0.25	-	900	23.6	50000	-23
			925	25.7	86100	-16
63	0.50	-	900	22.8	44000	-23
			925	25.5	77400	-13
64	1.00	-	900	22.4	46300	-15
			925	25.2	78000	+1
65	2.00	-	900	23.1	56600	0
			925	25.8	87600	-1
66	-	0.25	900	23.5	52000	-16
			925	25.3	84300	-15
67	-	0.50	900	23.6	46200	-6
			925	25.3	81700	-7
68	-	1.00	900	23.6	53700	-10
			925	25.2	79300	-5

69	-	2.00	900	24.5	56600	-12
			925	26.1	77200	-7
70	-	5.00	900	16.5	40000	-4
			925	25.1	60200	-4

In the embodiments 62~65 and 66~69, it is noted that the dielectric constant and the quality factor were higher when H₃BO₃ were added than B₂O₃, and especially, the stability of the temperature factor according to the sintering temperature was excellent, which testifies the effect of the present invention.

In the present invention, a high frequency dielectric ceramics composition may be constituted by combining a combination of (Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO₃ and yTiO₂ as a main component and one of 0~5 wt % B₂O₃, 0~5 wt % H₃BO₃, 0~5 wt % SiO₂-K₂O glass, 0~5 wt % B₂O₃ and SiO₂-K₂O glass, or 0~5 wt % H₃BO₃ and SiO₂-K₂O glass as an additive, which satisfies conditions of 0≤a≤1, 0≤b≤1, 0≤c≤1, 0≤d≤1 and 0≤y≤0.6.

INDUSTRIAL APPLICABILITY

As so far described, a high frequency dielectric characteristic having an excellent various temperature compensation varied according to the high quality factor, the dielectric constant and the stable temperature coefficient and composition but having a very low sintering temperature compared with the conventional dielectric composition can be implemented at a low-priced

material such as ZnO, MgO, CoO, NiO or TiO₂.

In addition, since Ag, Cu or their alloy or Ag/Pd alloy can be used as an internal electrode, and thus, can be used as various high frequency devices, i.e., a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low-temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

Especially, the low-temperature sintered composition obtains a remarkably high quality factor more than several times that of the conventional one.

10 In addition, combination of the almost infinite number of compositions exhibiting the excellent high frequency characteristic can be obtained in the composition range of the present invention.

CLAIMS

1. A high frequency dielectric ceramics composition constituted by combining a combination of $(\text{Zn}_{1-x}\text{M}_x)\text{TiO}_3$ and $y\text{TiO}_2$ as a main component, into
 5 which one of 0~5 wt % B_2O_3 , 0~5 wt % H_3BO_3 , 0~5 wt % $\text{SiO}_2\text{-K}_2\text{O}$ glass, 0~5 wt % B_2O_3 and $\text{SiO}_2\text{-K}_2\text{O}$ glass, or 0~5 wt % H_3BO_3 and $\text{SiO}_2\text{-K}_2\text{O}$ glass is added as an additive, satisfies conditions of

M is Mg, Co or Ni,

'x' is $0 \leq x \leq 0.55$ in case of Mg and 'x' is $0 \leq x \leq 1.0$ in case of Co, and
 10 $0 \leq x \leq 1.0$ in case of Ni, and

$0 \leq y \leq 0.6$.

2. A high frequency dielectric ceramics composition preparation method in which material powder of ZnO, MO (in this respect, MO is MgO, CoO
 15 or NiO) and TiO_2 is weighed according to a composition range of $(\text{Zn}_{1-x}\text{M}_x)\text{TiO}_3$ and $y\text{TiO}_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.55$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.6$), mixed and dried,

the dried powder is calcined at a temperature of 850~950°C,

the calcined powder is mixed with one of 0~5 wt % B_2O_3 , 0~5 wt %
 20 H_3BO_3 , 0~5 wt % $\text{SiO}_2\text{-K}_2\text{O}$ glass, 0~5 wt % B_2O_3 and $\text{SiO}_2\text{-K}_2\text{O}$ glass, or 0~5 wt % H_3BO_3 and $\text{SiO}_2\text{-K}_2\text{O}$ glass as an additive,

the mixed powder is crushed,

the crushed power is shaped,

the shaped body is fired at a temperature of 800~925°C, and

($Zn_{1-x}M_x$)TiO₃ is calcined at a temperature corresponding to a region (region II) of below a phase dissociation temperature as shown in Figure 1 to obtain ($Zn_{1-x}M_x$)TiO₃ (M is Mg, Co or Ni) of a single phase of rhombohedral/hexagonal crystal.

3. The method of claim 2, wherein the shaped body is made in a manner that an aqueous solution adding a PVA binder is sprayed onto the crushed powder to make a granule, to which a pressure is applied.

4. The method of claim 3, further comprises a step for maintaining the shaped body at a temperature of 300~500°C for a predetermined time and removing the binder.

5. The method of claim 2, wherein ($Zn_{1-x}M_x$)TiO₃ is first calcined, and the calcined ($Zn_{1-x}M_x$)TiO₃ is mixed with one of 0~5 wt % B₂O₃, 0~5 wt % H₃BO₃, 0~5 wt % SiO₂-K₂O glass, 0~5 wt % B₂O₃ and SiO₂-K₂O glass, or 0~5 wt % H₃BO₃ and SiO₂-K₂O glass as an additive, and then fired.

6. A high frequency dielectric ceramics composition constituted by combining a combination ($Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d}$)TiO₃ and yTiO₂ as a main component, into which one of 0~5 wt % B₂O₃, 0~5 wt % H₃BO₃, 0~5 wt % SiO₂-K₂O glass, 0~5 wt % B₂O₃ and SiO₂-K₂O glass, or 0~5 wt % H₃BO₃ and SiO₂-

K₂O glass is added as an additive, satisfies conditions of

$0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c \leq 1$, $0 \leq d \leq 1$ and

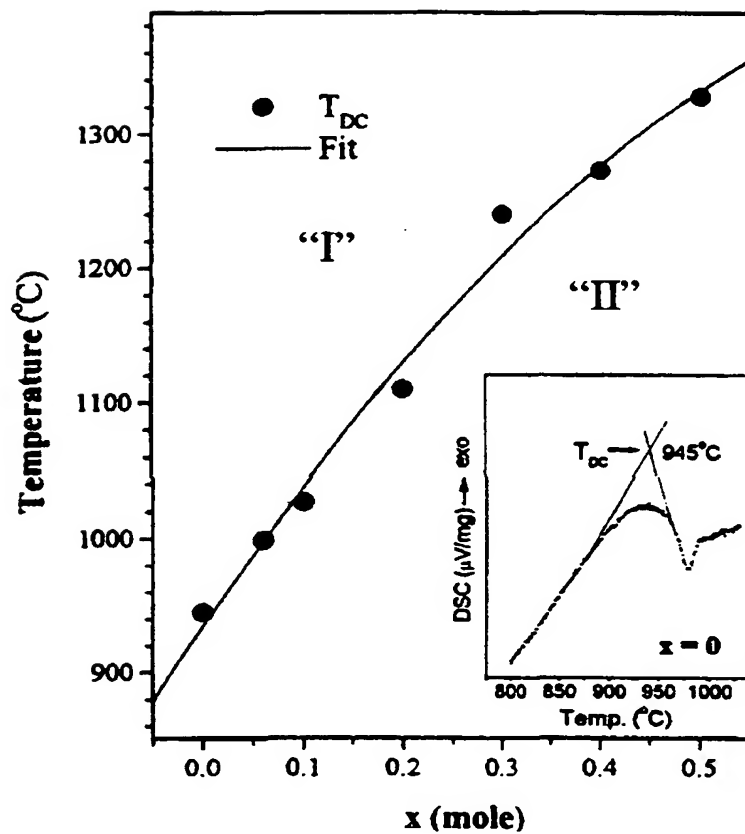
$0 \leq y \leq 0.6$.

- 5 7. Various high frequency devices such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a module, a low-temperature sintered substrate, a resonator and a filter or a ceramic antenna, are fabricated by using the dielectric composition of claim 1.

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FIG 1



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INTERNATIONAL SEARCH REPORT

 international application No.
 PCT/KR00/00984
A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C04B 35/46, H01B 3/12**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

korean patents and applications for inventions since 1975

korean utility models and applications for utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

N P S

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 06-312449 A(MARUWA CERAMIC) 21 NOVEMBER 1994 see the whole document	1 - 6
A	KR 93-0020437 A(KIM KYENG YONG) 04 OCTOBER 1993 see the whole document	1 - 6
A	KR 95-0045810 A(KITECH) 30 NOVEMBER 1995 see the whole document	1 - 6
A	KR 96-0050579 A(KAIST) 31 OCTOBER 1996 see the whole document	1 - 6

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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